

Vertical Profile of C, N, P, K and Radionuclides in Soil Collected from Highland Tea Plantation Areas

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Abstract: Problem statement: Cameron Highlands is a well known agricultural area in Peninsular Malaysia. Long term usage of fertilizer has caused accumulation of major elemental component in the soil. This accumulation will cause enrichment of the nutrient in the catchment located at downstream of the river through runoff. **Approach:** Two tea plantations on the upstream with hilly condition plantation were selected as the location for monitoring the accumulation of the major nutrient component N, P and K. C was also determined to estimate the total organic content in the soil. Natural radionuclides i.e., ²²⁶Ra, ²²⁸Ra and ⁴⁰K were also determined and anthropogenic radionuclides ¹³⁷Cs were detectable. The samples were measured using Elemental Analyzer, Energy Dispersive X-rays Fluorescence (EDXRF) and gamma spectrometer. The data set were analyzed using Principle Component Analysis (PCA) and Cluster Analysis (CA) to check the distribution and elemental sources. **Results:** The trend for all depth profile measurement results shown monotonically trend through the depth where it shown no observable trend except for C, N, P and ¹³⁷Cs decreasing through the depth. PCA results indicate that there are two sources for plantation A and three sources for plantation B that led to the accumulation of these elements. Three clusters of group element were found for both tea plantation area and the major sources are from fertilizer, natural occurring and atmospheric natural process. The model for C, N and P was found to be exponentially proportional to the depth with removing mixing layer. **Conclusion:** The range of concentrations for measured elements shows that the concentrations of elements in tea plantation B are higher than in tea plantation A. All depth profile gives monotonically trend except for C, N, P and ¹³⁷Cs since these elements were added to the soil. C, N and P are decreasing exponentially with depth. The amount of ¹³⁷Cs was found to be detectable for both study locations and it was from the fall out of nuclear explosion. Other radionuclides seem to be from natural existence and atmospheric natural process.

Key words: Soil erosion, soil profile, elemental analyzer, EDXRF, gamma spectrometry, vertical trend, cameron highlands, tea plantation, exponentially proportional, cultivated area

INTRODUCTION

Tea plantation in Cameron Highlands is a long life time plantation on high hill slopes that extended to more than 50 years. Long term usage of fertilizer had enriched the cultivated area with major component of fertilizer such as N, P and K in soil. The accumulated fertilizer that is not absorbed by the roots will be easily removed by runoff on the slope surface as well as leaching into the soil. Overused fertilizer will cause nonpoint pollution (Novotny *et al.*, 2010; Guo *et al.*, 2011; Carpenter *et al.*, 1998; Choudhury and Kennedy, 2005). Besides the normal major components chemical fertilizers of potash based and other type of fertilizer

also contained appreciable amount of radionuclides (Alam *et al.*, 1997; Chandrajith *et al.*, 2010; Favaro, 2005). The high hill of Cameron Highlands, Malaysia sit on the intermediate igneous rock mountain range (Ministry of Agriculture and Fisheries, 1970). Being igneous in origin the soil is known to contain natural radionuclides of uranium and thorium origins and ⁴⁰K (Ademola *et al.*, 2010; Anjos *et al.*, 2005; El-Arabi 2007; Moura *et al.*, 2011). With high altitude of more than 1100 m from sea level, it is suspected that the anthropogenic radionuclide ¹³⁷Cs also deposited in the soil (Lettner *et al.*, 2006; McGee *et al.*, 1992). With the hilly location up to 20° gradient steep slope, the runoff is much greater than flat area (Aminuddin *et al.*, 2005).

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Previous research at Cameron Highlands shows large amount of sediment accumulation at Sultan Abu Bakar Dam due to soil erosion (Hamzah *et al.*, 2011; Riduan *et al.*, 2009). The usage of fertilizer in Malaysia for industrial group including tea plantation has increased each year although without increased in the plantation's area (FAOUN, 2004). Tea plantations occupy 40% fraction of total agriculture area at Cameron Highlands (Aminuddin *et al.*, 2005). Without controlling the usage of fertilizer at tea plantation, the unused fertilizers will increase and also sweep by runoff.

MATERIALS AND METHODS

Sampling: Soil samples were collected at two tea plantations area in Cameron Highlands, Malaysia. The two locations are known as plantation A and plantation B. Seven sampling points were set at plantation A and six sampling point at plantation B and each sampling point location was determined using Global Positioning System (GPS). At each sampling point, ten profile soil samples up to 20 cm were taken as representative sample using hand auger. Each profile samples were sub-sampled at 2 cm slice. Two times drilling were necessary to get a profile up to 20 cm depth. Sub-sampled of the same layer was mix together. They were oven dried at 60°C until the constant weight achieved. The samples were then ground, homogenized and sieved using 250 µm sieve (Hamzah *et al.*, 2008). Each of the samples was stored in a plastic container, sealed and labeled.

Elemental Analyzer Measurement: C and N were determining using LECO CHNS-932 elemental analyzer. Each sample was weighted at 2.0 mg using micro balance into tin capsules. Five replicate for each sample was measured to maintain the consistent result. Standard sulphamethazine was used to calibrate the instrument. Blank sample was inserted between five replicates to flush the remaining contaminant before starting new sample measurement.

Energy Dispersive X-Ray Fluorescence (EDXRF) measurement: Pellet with 32 mm diameter and 2 mm thickness was prepared by pressing about 2 g of sample using fusion machine at 15 tonne pressure. Duplicate samples were prepared and measured using Minipal4 PANalytical bench-top EDXRF and the tube ratings were set to 300 mV, 150 µA with Rh target. Al-thin filter was used for measuring K, Mo filter for U and Th and no filter for P. K_{α} line was used in quantitative of P

and K at energy 2.013 keV and 3.312 keV, L_{α} line was used to measure U (13.612 keV) and Th (12.967 keV) with 100 second measuring time as optimize in our laboratory (Abdullah *et al.*, 2011). Standard calibration for P and K was carried out by using series of dilution of K_2HPO_4 , Standard Reference Material IAEA 312, IAEA 313, IAEA SL-1, IAEA Soil 7 and IAEA SL-1 for U and IAEA RG-Th-1 for Th (Hamzah *et al.*, 2011). Standard addition method was applied to soil samples to eliminate the matrix effect for P and K. The measurement conditions for standard and samples were set to be identical.

Gamma Spectrometer Measurement: About 400 g of samples was placed in plastic container, sealed and leaved for at least 3 weeks for the radionuclides in the samples to reach secular equilibrium state between parent and progenies (Alias *et al.*, 2008). Each sample was counted using HPGe detector for 12 h. The spectrums were analyzed using GammaVision software to determine the activity concentration of ^{226}Ra , ^{228}Ra , ^{40}K and ^{137}Cs .

Statistical analysis: To confirm the relationship between these elements, Pearson correlation were applied. Principal Component Analysis (PCA) and Cluster Analysis (CA) were used to identify whether the element came from same group perform using statistical analysis software XLSTAT.

RESULTS

Figure 1-10 show the average profile concentration of C, N, P, K and radionuclides in soil for plantations A and B. The Depth profile showed monotonic trend through the depth except for C, N, P and ^{137}Cs where it trend is decreasing through the depth. The concentration ranges of C, N, P, K, U, Th, ^{226}Ra , ^{228}Ra , ^{40}K and ^{137}Cs for plantations A and B are tabulated in Table 1.

Table 1: Range of concentrations and range of activity concentrations for elements and radionuclides

Element	Unit	Plantation A	Plantation B
C	mg/kg	669-30767	26950-85058
N	mg/kg	288.3-2338.3	1755.0-6162.5
P	mg/kg	936.6-2068.4	1251.8-4848.6
K	mg/kg	3859.3-4454.2	7275.4-7761.1
U	mg/kg	5.40-6.50	12.1-13.00
Th	mg/kg	27.3-30.50	56.9-71.10
^{226}Ra	Bq/kg	50.2-69.6	98.6-119.9
^{228}Ra	Bq/kg	97.4-124.0	186.2-253.2
^{40}K	Bq/kg	190.1-221.8	305.6-378.8
^{137}Cs	Bq/kg	0.68-1.47	0.86-1.99

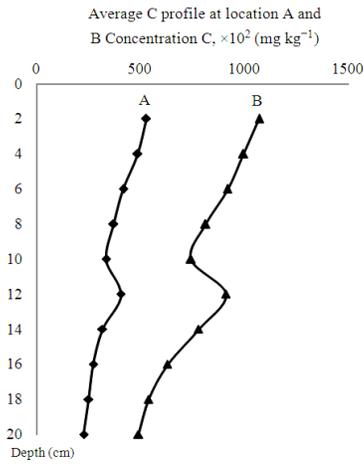


Fig. 1: Carbon profile

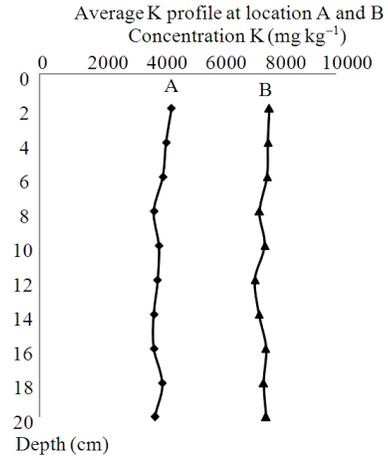


Fig. 4: Potassium profile

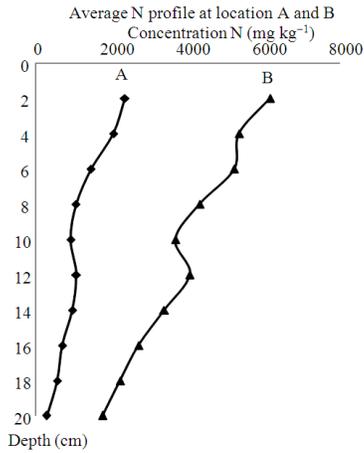


Fig. 2: Nitrogen profile

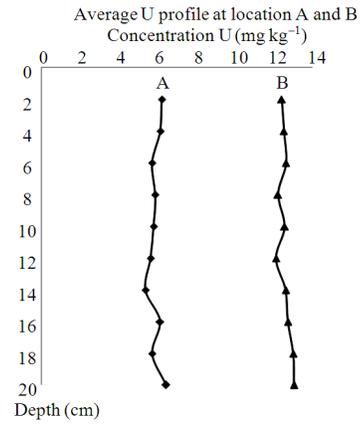


Fig. 5: Uranium profile

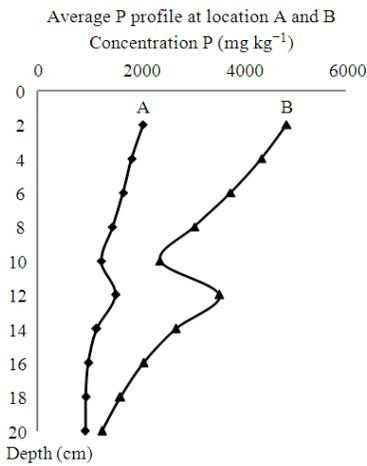


Fig. 3: Phosphorous profile

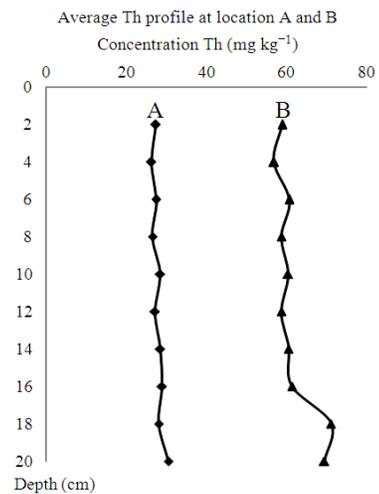


Fig. 6: Thorium profile

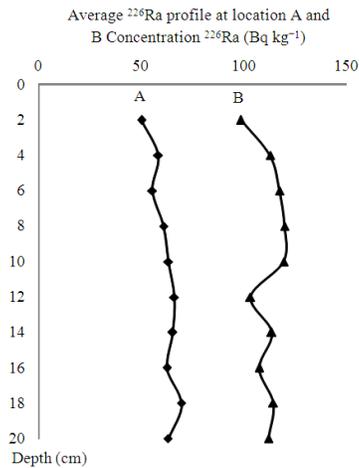


Fig. 7: ²²⁶Ra profile

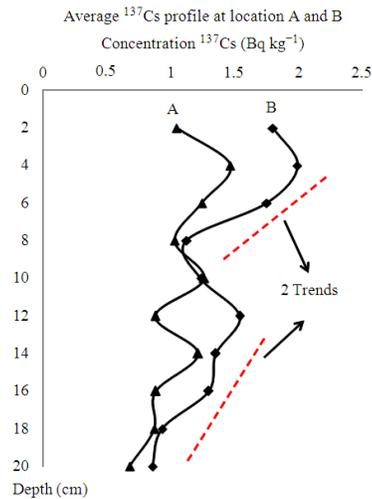


Fig. 10: ¹³⁷Cs profile

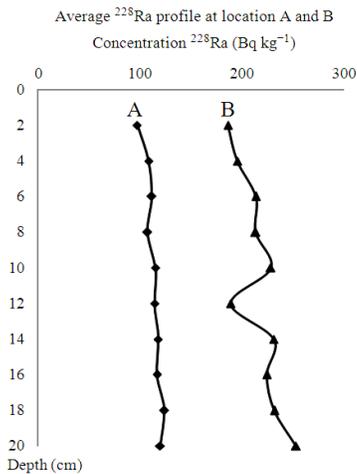


Fig. 8: ²²⁸Ra profile

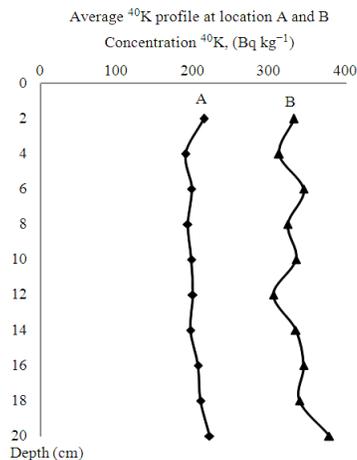


Fig. 9: ⁴⁰K profile

DISCUSSION

The concentration of C, N and P are decreasing through depth while K, U and Th are not changing very much with depth. The decreasing trend of these elements is due to natural process such as vertical leaching through the depth. Due to the external input from fertilizer on the top of the soil, the upper layer of the soil contains high concentration of N and P. For carbon, the bottom layer undergoes biodegradation and decomposition. The carbon content at the upper layer of soil is higher because of the input from decomposition of organic from leaf, root and other atmospheric deposition. The K show monotonic pattern through the depth, suggested that K is more soluble compare to the others element and the leaching process for K is much higher. Both plantations show different range where concentration at plantation B is much higher than plantation A for C, N, P and K. Although the range is different, the pattern of the depth profile show no significant different.

As for ¹³⁷Cs where it came from anthropogenic pollution through atmospheric fallout, it can be seen that (Fig. 10) there were two trends at 2-10 cm and 12-20 cm which suggested they were from nuclear weapon testing in year 1960s and Chernobyl nuclear accident 1986.

From Fig. 1-3, at layer 12 and 14 cm, the concentration of C, N and P is slightly higher than at 10 cm layer. The different is occurring due to the sample collection where the sample for profile was drilled twice at the same hole. Two times drilling is for layer 0-10 cm and 12-20 cm will introduce mixing layer at 12 cm and 14 cm. This mixing layer contributed to the observed high concentration at 12 and 14 cm depth.

Table 2: Pearson correlation coefficient between element and isotopes at plantation A

Variables	C	N	P	K	U	Th	²²⁶ Ra	²²⁸ Ra	⁴⁰ K	¹³⁷ Cs
C	1.000									
N	0.977	1.000								
P	0.995	0.964	1.000							
K	0.749	0.799	0.765	1.000						
U	0.108	0.121	0.156	0.237	1.000					
Th	-0.726	-0.707	-0.687	-0.451	0.276	1.000				
Ra-226	-0.852	-0.798	-0.884	-0.648	-0.418	0.331	1.000			
Ra-228	-0.915	-0.879	-0.916	-0.598	-0.275	0.596	0.879	1.000		
K-40	-0.369	-0.310	-0.310	0.082	0.554	0.717	-0.015	0.175	1.000	
Cs-137	0.656	0.622	0.621	0.379	-0.304	-0.585	-0.372	-0.376	-0.767	1

Table 3: Pearson correlation coefficient between element and isotopes at plantation B

Variables	C	N	P	K	U	Th	²²⁶ Ra	²²⁸ Ra	⁴⁰ K	¹³⁷ Cs
C	1									
N	0.986	1								
P	0.988	0.976	1							
K	0.266	0.258	0.368	1						
U	-0.629	-0.659	-0.543	0.468	1					
Th	-0.806	-0.780	-0.735	0.098	0.839	1				
Ra-226	-0.232	-0.238	-0.266	-0.061	0.216	0.148	1			
Ra-228	-0.809	-0.845	-0.796	0.036	0.785	0.739	0.524	1		
K-40	-0.569	-0.573	-0.508	0.433	0.812	0.709	0.172	0.807	1	
Cs-137	0.896	0.881	0.892	0.290	-0.508	-0.761	-0.352	-0.812	-0.569	1

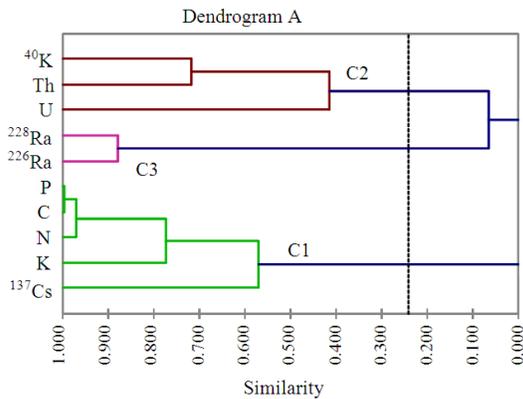


Fig. 11: Dendrogram plantation A

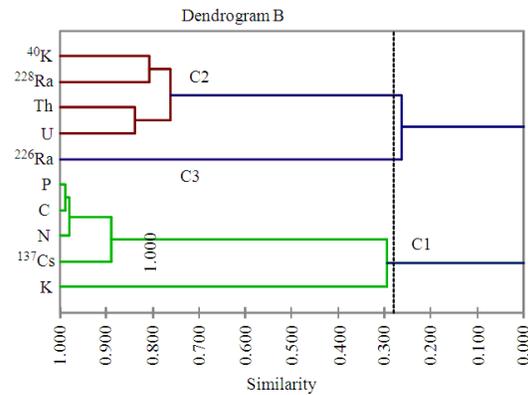


Fig. 12: Dendrogram plantation B

Pearson correlation between elements are shown in Table 2 and 3 while dendrogram for plantation A and B are shown in Fig. 11 and 12. It shows that strong correlation between C, N, P and K for plantation A and B except for K at plantation B. Dendrogram show that C, N, P, K and ¹³⁷Cs was clustered as C1 group for A and B. U, Th, ²²⁶Ra, ²²⁸Ra and ⁴⁰K also clustered as group C2 and C3 as we expect it is from natural origin.

Principal Component Analysis was applied to the whole set data separately for plantation A and plantation B. There are two principal components for plantation A and three principal components for plantation B referring eigenvalues that exceed 1. Plantation A counted for 61.98 and 23.28% of total variation data. Plantation B counted for 64.41%, 18.68 and 10.02% of total variation data respectively with a total cumulative of 85.26 % and 93.11% for plantations A and B. For plantation A, five elements were related to factor 1 in positive direction and three elements in negative direction. C, N, P, K and ¹³⁷Cs were related to positive factor and Th, ²²⁶Ra and ²²⁸Ra related to negative factor. U, Th and ⁴⁰K are related to factor two.

For plantation B, factor one is related for element C, N, P and ¹³⁷Cs. Factor two were strongly for element K, U and ⁴⁰K. ²²⁶Ra were strongly related to factor three.

Cluster Analysis (CA) for both plantation (Fig. 11 and 12), cluster C1 group of element consist of C, N, P and ¹³⁷Cs was observed for both plantation due to their trend profile that decreasing through the depth and as the elements that added to the soil. The sources of this element suggested it from fertilizer application except

for ^{137}Cs which it from anthropogenic pollution from atmospheric deposition.

U, Th and ^{40}K was clustered as C2 group for both plantations. ^{226}Ra was clustered into C3 group and ^{228}Ra in C2 group for plantation B. ^{226}Ra and ^{228}Ra for plantation A was clustered in C3 group. C2 and C3 group was suggested come from natural occurring and atmospheric natural process. The clustering ^{228}Ra at C3 for Plantation B and C3 at plantation A maybe attributed to the different of altitude, slope, soil type and soil densities of the two study location.

As we observe the trend of C, N and P is decreasing through the depth, we plot an exponential trendline to get the trend within the depth. The correlation coefficient of the exponential is in a good agreement with depth with R^2 more than 0.9 by removing mixing layer.

CONCLUSION

In general the range of elemental concentration at plantation B is higher than plantation A. All depth profile give monotonically trend except for C, N, P and ^{137}Cs where elements were added to the soil which when applying fertilizer and it may originated from atmospheric process. The concentration of C, N and P are decreasing exponentially with depth. ^{137}Cs was found at low activity concentration at study locations. Other radionuclide's ^{226}Ra , ^{228}Ra and ^{40}K seem to be from natural existence and atmospheric natural process. Except for ^{228}Ra , all elements are clustered in their identical respective cluster in both plantation A and B.

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REFERENCES

Abdullah, M.Z., A. Saat and Z. Hamzah, 2011. Optimization of energy dispersive X-Ray fluorescence spectrometer to analyze heavy metals in moss samples. *Am. J. Eng. Applied Sci.* 4: 355-362. DOI: 10.3844/ajeassp.2011.355.362
Ademola, J.A., and A.A. Ayeni. 2010. Measurement of natural radionuclides and dose assessment of granites from Ondo State, Nigeria.

Radioprotection, 45: 513-521. DOI: 10.1051/radiopro/2010046
Alam, M.N., M.I. Chowdhury, M. Kamal, S. Ghose and H. Banu *et al.*, 1997. Radioactivity in chemical fertilizers used in Bangladesh. *Applied Radiation Isotopes*, 48: 1165-1168. DOI: 10.1016/S0969-8043(97)00019-5
Alias, M., Z. Hamzah, A. Saat, M. Omar and A.K. Wood. 2008. An Assessment of absorbed dose and radiation hazard index from natural radioactivity. *Malaysian J. Anal. Sci.*, 12: 195-204.
Aminuddin, B.Y., M.H. Ghulam, W.Y.W. Abdullah, M. Zulkefli and R.B. Salama, 2005. Sustainability of current agricultural practices in the Cameron Highlands, Malaysia. *Water, Air Soil Poll., Focus*, 51: 89-101. DOI: 10.1007/s11267-005-7405-y
Anjos, R.M., R. Veiga, T. Soares, A.M.A. Santos and J.G. Aguiar, *et al.*, 2005. Natural radionuclide distribution in brazilian commercial granites. *Radiation Measur.*, 39: 245-253. DOI: 10.1016/j.radmeas.2004.05.002
Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth and A.N. Sharpley *et al.*, 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecolog. Applied*, 8: 559-568. DOI: 10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2
Chandrajith, R., S. Seneviratna, K. Wickramaarachchi, T. Attanayake and T. Aturaliya *et al.*, 2010. Natural radionuclides and trace elements in rice field soils in relation to fertilizer application: study of a chronic kidney disease area in Sri Lanka. *Environ. Earth Sci.*, 60: 193-201. DOI: 10.1007/s12665-009-0179-1
Choudhury, A.T.M.A. and I.R. Kennedy, 2005. Nitrogen fertilizer losses from rice soils and control of environmental pollution problems. *Commun. Soil Sci. Plant Anal.*, 36: 1625-1639. DOI: 10.1081/CSS-200059104
El-Arabi, A.M., 2007. ^{226}Ra , ^{232}Th and ^{40}K concentrations in igneous rocks from eastern desert, Egypt and its radiological implications. *Radiation Measur.*, 42: 94-100. DOI: 10.1016/j.radmeas.2006.06.008
FAOUN, 2004. Fertilizer use by crop in Malaysia. Rome.
Favaro, D.I.T., 2005. Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil. *J. Radioanalyti. Nuclear Chem.*, 264: 445-448. DOI: 10.1007/s10967-005-0735-4

- Guo, Z., C. He, Y. Ma, H. Zhu and F. Liu *et al.*, 2011. Effect of different fertilization on spring cabbage (*Brassica oleracea* L. var. *capitata*) production and fertilizer use efficiencies. *Agric. Sci.*, 2: 208-211. DOI: 10.4236/as.2011.23029
- Hamzah, Z., A. Saat, N.H. Mashuri and S.D. Redzuan, 2008. Surface radiation dose and radionuclide measurement in ex-tin mining area, Kg Gajah, Perak. *Malaysian J. Anal. Sci.*, 12: 419-431.
- Hamzah, Z., S.D. Riduan and A. Saat, 2011. Determination of sediment profile for ^{210}Pb , Pb, U and Th from sultan Abu Bakar dam due to soil erosion from highland agriculture area, Cameron Highlands, Malaysia. *Am. J. Environ. Sci.*, 7: 263-268. DOI: 10.3844/ajessp.2011.263.268
- Lettner, H., A. Griesebner, T. Peer, A.K. Hubner and M. Pintaric, 2006. Altitude dependent ^{137}Cs concentrations in different plant species in alpine agricultural areas. *J. Environ. Radioactivity*, 86: 12-30. DOI: 10.1016/j.jenvrad.2005.06.007
- McGee, E.J., P.A. Colgan, D.E. Dawson, B. Rafferty and C. O'Keeffe, 1992. Effects of topography on caesium-137 in montane peat soils and vegetation. *Analyst*, 117: 461-464. DOI: 10.1039/AN9921700461
- Ministry of Agriculture and Fisheries, 1970. Generalized Soil Map Peninsular Malaysia 1970. Direktorat Pemetaan Negara, Malaysia No-137-1976, 1: 800000, Kuala Lumpur.
- Moura, C., A. Artur, D. Bonotto, S. Guedes and C. Martinelli, 2011. Natural radioactivity and radon exhalation rate in Brazilian igneous rocks. *Applied Radiation Isotopes*, 69: 1094-1099. DOI: 10.1016/j.apradiso.2011.03.004
- Novotny, V., X. Wang, A. Englande, D. Bedoya and L. Promakasikorn *et al.*, 2010. Comparative assessment of pollution by the use of industrial agricultural fertilizers in four rapidly developing Asian countries. *Environ. Dev. Sustain.*, 12: 491-509. DOI: 10.1007/s10668-009-9207-2
- Riduan, S.D., Z. Hamzah and A. Saat, 2009. In-situ measurement of selected water quality parameters in ringlet's lake, cameron highlands. *Malaysian J. Chem.*, 11: 122-128.